AD-A042 525   ARMY ELECTRONICS COMMAND FORT MONMOUTH N J   F/G 11/9

RADIATION DEGRADATION SUSCEPTIBILITY OF SEVERAL RELATED POLYMER--ETC(U)

JUL 77 J N HELBERT, E H POINDEXTER, G A STAHL

UNCLASSIFIED   ECOM-4504   NL

| OF |

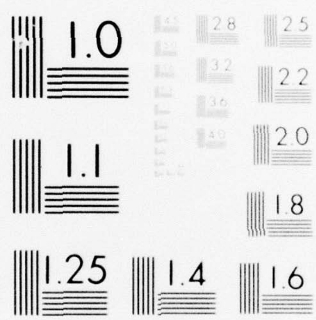
AD A042525

END

DATE FILMED

8-77

DDC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

Research and Development Technical Report

ECOM-4504

RADIATION DEGRADATION SUSCEPTIBILITY OF SEVERAL RELATED POLYMERS

J. N. Helbert
E. H. Poindexter
Electronics Technology & Devices Laboratory

G. A. Stahl
R. C. Chen
C. U. Pittman, Jr.
University of Alabama

July 1977

ECOM

US ARMY ELECTRONICS COMMAND FORT MONMOUTH, NEW JERSEY 07703

NOTICES

Disclaimers

Disposition

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: (14) ECOM-4504 (9) Research and development	2. GOVT ACCESSION NO. / 3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle): (6) RADIATION DEGRADATION SUSCEPTIBILITY OF SEVERAL RELATED POLYMERS.	5. TYPE OF REPORT & PERIOD COVERED: technical rept.,
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): (10) J.N. Helbert, E.H. Poindexter, G.A. Stahl, R.C. Chen, C.U. Pittman, Jr. University of Alabama	8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Electronic Materials Research Technical Area, US Army Electronics Technology & Devices Lab, Fort Monmouth, NJ 07703 DRSEL-TL-EC	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 61102A (16) 1L161102AH47 (17) S7 011
11. CONTROLLING OFFICE NAME AND ADDRESS: US Army Electronics Command, DRSEL-TL-EC, Fort Monmouth, NJ 07703	12. REPORT DATE: (11) July 1977
	13. NUMBER OF PAGES: 5 (12) 9p.
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

This paper was presented at the 173rd National Meeting, American Chemical Society, New Orleans, March 1977; also published in Polymer Preprints, Vol 18, No. 1, March 1977.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Radiation degradation
Polymers

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Radiation degradation is observed for irradiated poly(methyl alpha-chloroacrylate) (PMCA), poly(methacrylonitrile)(PMCN), and poly(methyl methacrylate)(PMMA) by gel permeation chromatography (GPC). Molecular weight averages obtained by GPC on irradiated sample solutions indicate cross-linking also occurs in irradiated PMCA and PMCN. G(s) is determined to be 6-8 and G(x) 1-2 for PMCA, while ((G(s)-G(x)) is 2.1 for irradiated PMCN. GPC data for irradiated poly (methacrylic anhydride) and poly(acrylic anhydride) model polymers indicate that these polymers are less sensitive to radiation degradation than the (contd)

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

037620

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

20. Abstract (contd)

related polymers. The combination of results suggests that the main-chain scission process is not initiated by decarboxylation, but by a mechanism involving methylene radicals produced by C-H bond dissociation on the ester-methyl or alpha-methyl polymer groups.

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

CONTENTS

TABLES

RADIATION DEGRADATION SUSCEPTIBILITY OF SEVERAL RELATED POLYMERS

by

J. N. Helbert and E. H. Poindexter
US Army Electronics Technology and Devices Laboratory (ECOM)
Fort Monmouth, New Jersey 07703

G. A. Stahl, R. C. Chen, and C. U. Pittman, Jr.
University of Alabama
University, Alabama 35486

INTRODUCTION

The use of radiation degrading and cross-linking polymers as electron-beam[1] and x-ray[2] resists has led to renewed interest in the radiation chemistry of polymers. Additional interest is found in textile and other industries,[3] where polymers that radiation degrade or graft have potential in prototype radiation processing of products.

In this paper, we present evidence of radiation degradation for poly (methyl methacrylate)(PMMA), poly(methacrylonitrile)(PMCN), and poly(methyl alpha-chloroacrylate)(PMCA) as determined by molecular weight decreases observed by gel permeation chromatography (GPC). GPC chromatograms of γ-irradiated poly(methacrylic anhydride)(PMAAN) and poly(acrylic anhydride)(PAAN) were also obtained and analyzed as model polymers. Intrinsic viscosities were determined for each irradiated anhydride sample.

EXPERIMENTAL

Polymer samples were synthesized by methods outlined by Sorenson.[4] Samples were irradiated in 5-mm OD pyrex tubes evacuated to $< 10^{-3}$ micron. Irradiations were carried out with a ^{60}Co gamma-ray source employing dose rates of 0.01-0.8 Mrad/hr.

GPC measurements were made with a Waters Model 201 GPC chromatograph equipped with micro-styrogel columns; chloroform and DMF were employed as mobile phases. Electron paramagnetic resonance (EPR) measurements were made with a Varian Model 4500 spectrometer at 77°K. Intrinsic viscosities were measured with a dilution Ubbelohde viscometer for DMF anhydride solutions.

RESULTS

GPC chromatograms for irradiated PMMA, PMCN, and PMCA shift to longer elution times with increasing dose. Increasing $\bar{M}_N^{-1}$ values (i.e., decreasing $\bar{M}_N$) are listed for these irradiated polymers in Table I. Absolute molecular weights are calculated by the Q-factor method, where Q is obtained for the unirradiated polymers by membrane osmometry. Relative molecular size changes were obtained via polystyrene standard molecular weight calibration under equivalent conditions.

In contrast to the methacrylate polymers above, GPC chromatograms of irradiated PAAN shift to slightly longer elution times only for the range of doses below one Mrad, then move to shorter elution times with increasing sample dose. Chromatograms of PMAAN samples undergo similar changes for doses $\leq$ 2.5 Mrad, but remain unchanged at doses > 7 Mrad. Decreases in intrinsic viscosities for dissolved aliquots of the same irradiated PMAAN samples decrease until about 7 Mrad. Consistent with the GPC data, the intrinsic viscosities for the irradiated PAAN samples decrease until 1-2 Mrad, then continually increase to 48 Mrad, the highest dose studied. A tabulation of the essential data are found in Tables II and III.

From the slope of a plot of M_N^{-1} versus dose in Mrad, rates of radiation events per unit dose may be obtained. G(number of scissions/100 eV), G(s),

G(number of cross-links/100 eV) G(x), or [G(s)-G(x)], values may be obtained.[5,6] In degrading polymer cases where G(x) is established to be zero (e.g., PMMA), G(s) is obtained. Observation of G(x)=0 for degrading polymers is quite rare, thus the latter quantity is usually obtained and reported. [G(s)-G(x)] values quantitatively characterize the polymer on the basis of the dominating process, but say little of the absolute magnitudes of the G values involved. Tables I and II contain [G(s)-G(x)] values obtained in this work.

The EPR spectrum of γ-irradiated PMCA at 77°K is an anisotropically broadened triplet[7] with hyperfine splitting of a^H=22±1 gauss. Upon warming, the radical spectrum decays below detection. G(radicals/100 eV dose), G(rads), versus PMMA G(rads)=1.6[8] is determined to be 5.7±1.2.[7]

DISCUSSION

Radiation degradation is observed for PMCA, PMCN and PMMA homopolymers. [G(s)-G(x)] values from Table I, suggest that the PMCA and PMCN polymers are slightly more or as sensitive to radiation degradation as PMMA. A [G(s)-G(x)] value of 9.6 (versus PMMA [G(s)-G(x)] = 2.3; G(x)=0) has been previously reported.[9] It was calculated from the slope of M_N^{-1} versus dose obtained by membrane osmometry. Normalizing this value to the PMMA [G(s)-G(x)] value obtained in this work of 1.9, we obtain [G(s)-G(x)] = 7.9±0.8, which is in fair agreement with [G(s)=G(x)] = 6.7±0.8 obtained here. Since no other radicals are observed other than the scission precursor radical in irradiated PMCA, G(rads) may be taken to be approximately equal to G(s). Based upon the results of the three independent measurements, G(s) is established to be 6-8 and G(x) about 1-2 for PMCA. Further evidence for the occurrence of radiation cross-linking and the appreciable magnitude of G(x) is found in the M_W/M_N values listed in Table I. In cases where G(x)=0, the M_W/M_N ratio approaches 2 at high doses[10]; M_W/M_N for PMCA does not approach 2 and is still as high as 2.9 at a dose of 48 Mrad as compared to 2.6 for the original unirradiated polymer.

The triplet EPR spectrum observed for irradiated PMCA could be assigned to either of the radicals with structures $-CH_2-C(Cl)(CO_2\dot{C}H_2)-$ or $-CH_2-\dot{C}(Cl)(CO_2CH_3)$. The observed EPR splitting constant of 22 gauss is similar to that of 19 gauss observed for irradiated PMMA; the radical structure assigned to that EPR triplet is $-CH_2-C(CH_3)(CO_2\dot{C}H_2)-$.[11] Considering this and the fact that the $-CH_2-\dot{C}(Cl)(CO_2CH_3)$ would have to result from a direct main-chain scission process which is held to be unfavorable due to the "cage effect" in ref. 11 for PMMA, we assign the former radical structure to the observed triplet in irradiated PMCA.

The results of Table II for the anhydrides are interesting. These anhydride polymers differ from PMMA and poly(methyl acrylate)(PMA) only in the ester anhydride bridging. One might predict irradiated PMAAN to degrade as PMMA does and irradiated PAAN to cross-link as PMA does. Cross-linking is observed for PAAN over doses of 2-48 Mrad as determined by M_N^{-1} decreases and intrinsic viscosity increases (see Tables II and III). Degradation is observed for PMAAN over the dose range of 0-5 Mrad, but M_N^{-1} is very constant from about 7-19 Mrad thus indicating that G(s)≅G(x) over that dose range. Strangely, radiation degradation is also observed for irradiated PAAN up to 1-1.5 Mrad. This degradation, however, is probably not too effective due to a large increase in M_W/M_N ratio, which is an indication of a simultaneous cross-linking process. The degree of early degradation is, therefore, of scant consequence for PAAN and the polymer generally behaves to ionizing radiation in a cross-linking mode. Although degradation appears to be more favorable in the PMAAN polymer as observed by the M_N^{-1} increases and intrinsic viscosity decreases over larger ranges than for PAAN, this polymer is also rather insensitive to radiation as far as molecular weight changes are concerned.

The striking radiation behavior of the model anhydride polymers leads one to doubt seriously any proposed free radical mechanism for main-chain scission where the initiating event is ester side-group cleavage followed by molecular rearrangement. The results presented here favor a free radical main-chain scission mechanism where the initiating event is a C-H bond cleavage, either at the ester methyl or the alpha-methyl groups induced by the energy absorptive interaction of the Compton electrons produced by early ionization events.

SUMMARY

EPR results for irradiated PMCA hint at a free radical mechanism for main-chain scission in that polymer. This mechanism probably follows the initial ionization event where ester group cleavage apparently occurs along with high-energy Compton electron ejection. It is the Compton electrons, then, that produce the free radical precursor of the main-chain scission events in both PMMA and PMCA. Lack of unambiguous detection of the radicals $-CH_2-\dot{C}(CH_3)-$[11] and $\cdot CO_2CH_3$[12] is in accord with this proposed mechanism.

PMCN like PMCA, PMMA, and other polymers with monomer repeat unit $-CH_2-C(X)Y-$(X and Y+H) is a degrading polymer. Larger increases in the M_W/M_N ratio over the employed dose range (see Table I) for this polymer than for PMMA of roughly equivalent initial M_W/M_N, is evidence of simultaneous cross-linking and $G(x)>0$ for this polymer as found also for PMCA.

REFERENCES

1. (a) A.N. Broers and M. Hatzakis, Scientific American, November (1972).
   (b) L.F. Thompson, Solid State Tech., 27, July (1974).
   (c) L.F. Thompson, Solid State Tech., 41, August (1974).

2. L.F. Thompson, E.D. Feit, M.J. Bowden, P.V. Lenzo, and E.G. Spencer, J. Electrochem. Soc., 121, 1500 (1974).

3. J.E. Wilson, "Radiation Chemistry of Monomers, Polymers, and Plastics," Marcel Dekker, Inc., New York, 1974.

4. W.R. Sorenson and T.W. Campbell, "Preparative Methods of Polymer Chemistry," Interscience, New York, 1968.

5. A. Charlesby, "Atomic Radiation and Polymers," Pergamon Press, London, 1960.

6. M. Dole, "Radiation Chemistry of Macromolecules," Academic Press, New York, Vol. II, 1973.

7. J.N. Helbert, B.E. Wagner, P.J. Caplan, and E.H. Poindexter, J. of Appl. Polym. Sci., 13, 825 (1975).

8. M. Omerod and A. Charlesby, Polymer, 5, 67 (1964).

9. J.N. Helbert, P.J. Caplan, and E.H. Poindexter, J. of Appl. Polym. Sci., 21 (1977). (In press).

10. N.S. Viswanathan, J. of Polym. Sci., 14, 1553 (1976).

11. G. Geuskens and C. David, Die Makromolekulare Chemie, 165, 273 (1973).

12. A. Torikai, H. Kato, and Z-I. Kuri, J. of Polym. Sci., Chem. Ed., 14, 1065 (1976).

TABLE I: M_N^{-1}, M_W/M_N, and $\left[G(s)-G(x)\right]$ values for irradiated PMCA, PMMA, and PMCN.

Polymer	Dose, Mrad	$M_N^{-1} \times 10^5$	M_W/M_N	Initial $\left[G(s)-G(x)\right]$
PMCA	0	0.80	2.6±0.2	6.7±0.8
	0.72	1.4	3.1	
	1.4	1.8	3.0	
	2.1	1.9	2.6	
	49	4.2	2.9	
PMMA	0	2.9	1.1±0.1	1.9±0.3
	0.7	3.1	1.1	
	1.4	3.2	1.1	
	9.7	4.9	1.2	
	87	18	1.4	
PMCN	0	1.9	1.04±0.05	2.1±0.3
	1.4	2.4	1.08	
	3.3	2.8	1.12	
	11.8	4.5	1.30	
	49	6.2	1.40	

TABLE II: M_N^{-1} and M_W/M_N, and $[G(s)-G(x)]$ values for irradiated PMAAN and PAAN polymers.

Polymer	Dose, Mrad	$M_N^{-1}x10^7$	M_W/M_N	Initial $[G(s)-G(x)]$
PMAAN	0	5.9	1.2±0.1	0.4±0.2
	0.96	9.9	2.7	
	2.5	9.7	3.1	
	4.9	8.0	1.9	
	9.9	7.4	1.9	
	19	7.4	1.9	
PAAN	0	2.4	2.6	0.9±0.4
	0.96	8.4	4.0	
	2.3	3.6	1.9	
	4.7	3.1	1.9	
	9.5	1.2	1.7	

TABLE III: Intrinsic viscosities for irradiated PMAAN and PAAN polymer samples measured in DMF.

Polymer	Dose, Mrad	$[\eta]$, dl/gm
PMAAN	0	0.55
	2.5	0.52
	4.9	0.49
	9.9	0.46
	19	0.50
	49	0.52
PAAN	0	0.54
	2.3	0.53
	4.7	0.58
	9.5	0.61
	48	0.73